Short communication

Improvement of electrochemical performance in alkaline fuel cell by hydroxide ion conducting Ni–Al layered double hydroxide

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HIGHLIGHTS

► Layered double hydroxides (LDHs) were used as ionomer of an alkaline fuel cell.
► Ni–Al and Mg–Al LDH intercalated with CO_3^{2-} were added to the catalyst layer.
► The catalyst layer with LDHs showed better performance than that without LDHs.
► OH^- conductive LDHs contribute to constructing more favorable triple phase boundary regions.

ARTICLE INFO

ABSTRACT

This paper reports on the application of hydroxide ion conducting layered double hydroxides (LDHs) to the catalyst layer in an alkaline fuel cell for the improvement of the oxygen reduction reaction (ORR) at the triple phase boundary (TPB) in the catalyst layer. Ni–Al LDH intercalated with CO_3^{2-} (Ni–Al CO_3^{2-} LDH) and Mg–Al CO_3^{2-} LDH were used in this study. Ni–Al CO_3^{2-} LDH showed higher ionic conductivity than Mg–Al CO_3^{2-} LDH under R.H. of 80%. The catalyst layers with and without hydroxide ion conducting LDHs was prepared, and a half-cell using the prepared catalyst layers was fabricated. The addition of LDHs to the catalyst layer increased the reduction current for ORR, indicating that hydroxide ion conducting LDHs introduced OH^- conducting paths and increased TPB region within the catalyst layer. Above all, the addition of Ni–Al CO_3^{2-} LDH to the catalyst layer more effectively increased the reduction current for ORR than the addition of Mg–Al CO_3^{2-} LDH. The performance of the alkaline-type direct ethanol fuel cell was also improved. These experimental results indicate that high hydroxide ion conducting Ni–Al CO_3^{2-} LDH effectively increased TPB region within the catalyst layer.

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1. Introduction

Alkaline fuel cells (AFCs) with electrolytes such as KOH aqueous solution show a higher performance in well-known low-temperature fuel cells such as polymer electrolyte membrane fuel cell (PEMFC) and direct alcohol fuel cell (DAFC), and have received attention in recent years [1–3]. This is mainly due to faster kinetics for oxygen reduction reaction (ORR). In addition to the advantage, the cost of AFCs will be lower than that of other cells due to the possible use of non-platinum catalyst such as nickel and silver [4–6]. However, as one of the serious issues of AFC, it is well known that KOH aqueous solution used as the electrolyte is very sensitive to the presence of carbon dioxide. The formation of solid carbonate salts in the electrolyte or electrode/electrolyte interface causes the degradation of the cell performance [7–9]. The effect of carbon dioxide is much small in a solid electrolyte such as anion exchange

membrane (AEM). Therefore, researches have recently focused on the development of AFCs using solid electrolytes [2,10–12].

Fuel cell reactions mainly occur at triple phase boundary (TPB) regions that are formed by three phases; catalysts, ion conductors, reactants. Thus, the TPB regions are very important in determining the cell performance. However, in fuel cells using a solid electrolyte, it is difficult to form the TPB regions within the catalyst layer of electrodes because the electrode/electrolyte interface is solid-solid interface. Although Nafion acts as proton conducting ionomer and drastically improves the cell performance in PEMFC, sufficient materials, ionomers, to effectively transport OH^- ions have not been found in AFC at present.

We have focused attention on layered double hydroxides (LDHs) as an ion conducting material. LDHs are anionic clay and the general formula for LDHs is $[M^{II}_{1-x}M^{III}_x(OH)_2][(A^{n-})_{x/n} \cdot mH_2O]$, where M^{II} is a divalent cation such as Ni^{2+}, Mg^{2+}, Zn^{2+}, etc., and M^{III} is a trivalent cation such as Al^{3+}, Fe^{3+}, Cr^{3+}, etc., and A^{n-} is an anion such as CO_3^{2-}, Cl^-, OH^-, etc. In LDHs, divalent cations in the hydroxide layer are replaced with trivalent cation and the

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replacement of divalent cation with trivalent cation generates a positive charge on the hydroxide layers of LDHs. LDHs consist of the positively charged metal hydroxide layers with anions located in the interlayer space for charge compensation of the cationic layers. We have recently reported that the ionic conductivity of LDHs are closely related to the species of intercalated anions, LDHs intercalated with CO_3^{2-} showed high hydroxide ion conductivity of the order of 10^{-3} S cm^{-1} under 80% relative humidity [13–16]. We also reported that LDHs are hydroxide ion conductor, and can be applied to the solid electrolyte of alkaline direct ethanol fuel cell (DEFC) [13,15,16]. Electrochemical applications of LDH to electrochemical sensor, electrocatalyst and super capacitor were also reported [17–20]. In the fuel cell application, Ganley et al. added Ni–Al LDH as catalytic promoter to the electrolyte membrane/electrocatalyst interface [21]. Miyazaki et al. added Mg–Al CO_3^{2-} LDH and Ni–Al Cl$^-$ LDH to the cathode catalyst layer for construction more favorable TPB region, and concluded that the addition of Mg–Al CO_3^{2-} LDH to the catalyst layer more effectively improved the electrochemical performance of cathode than Ni–Al Cl$^-$ LDH [22]. We have been studying hydroxide ion conduction in LDHs. Thus, we studied the application of LDHs with high hydroxide ion conductivity to the catalyst layer of AFC.

In the present study, Ni–Al CO_3^{2-} LDH and Mg–Al CO_3^{2-} LDH were prepared, and the structure and electrochemical properties of Ni–Al CO_3^{2-} LDH and Mg–Al CO_3^{2-} LDH were examined. Then, the catalyst layers with and without LDHs as an ionomer were prepared and the ORR activity of the prepared catalyst layers was evaluated by a half-cell using the prepared catalyst layers and an anion exchange membrane. In addition, to evaluate how LDHs affected the TPB regions in the catalyst layers and cell performances, DEFCs using the prepared catalyst layers were fabricated and evaluated.

2. Experimental

2.1. Preparation and structural characterization of LDHs

Ni–Al LDH intercalated with CO_3^{2-} (Ni–Al CO_3^{2-} LDH) was prepared by using the co-precipitation method reported by Miyata [23]. Ni(NO$_3$)$_2$·6H$_2$O and Al(NO$_3$)$_3$·9H$_2$O were dissolved in deionized water in a molar ratio of 3:1 (Ni:Al). The mixture was dropped into 0.3 M Na$_2$CO$_3$ solution with stirring at 80 °C. The pH of the reaction mixture was adjusted to 10 by the addition of 2 M NaOH solution and the mixture was aged at 80 °C for 17 h. Then, the resulting green precipitates were filtrated, washed with distilled water, and dried at 80 °C. Mg–Al CO_3^{2-} LDH was prepared in the same way as Ni–Al CO_3^{2-} LDH.

X-ray diffraction (XRD) patterns were measured to identify crystalline phases. The morphology of prepared LDHs was observed using a field-emission-type scanning electron microscope (FE-SEM, S4500, Hitachi). The surface area of the prepared LDHs was determined using BET surface area analysis.

The electrical conductivities of LDHs were investigated using impedance data in a frequency range from 1 Hz to 8 MHz (Solartron 1260; Solartron Analytical). Pellets of Ni–Al LDHs for electrical conductivities were obtained by the cold pressing under 200 MPa. Gold was sputtered as the electrodes on both sides of the pelletized Ni–Al LDHs. The electronic conductivity of Ni–Al CO_3^{2-} LDH was also investigated by a DC polarization technique.

2.2. Evaluation of the ORR activity of catalyst layers with LDHs

Effects of LDHs to the TPB regions in catalyst layers were evaluated using a half cell using an AEM (AHA; Tokuyama Corp.) as presented in Fig. 1 [22]. The catalyst inks were prepared by mixing Pt/C (EC-20-10-10; Electrochem Inc.), LDH and PTFE as a binder
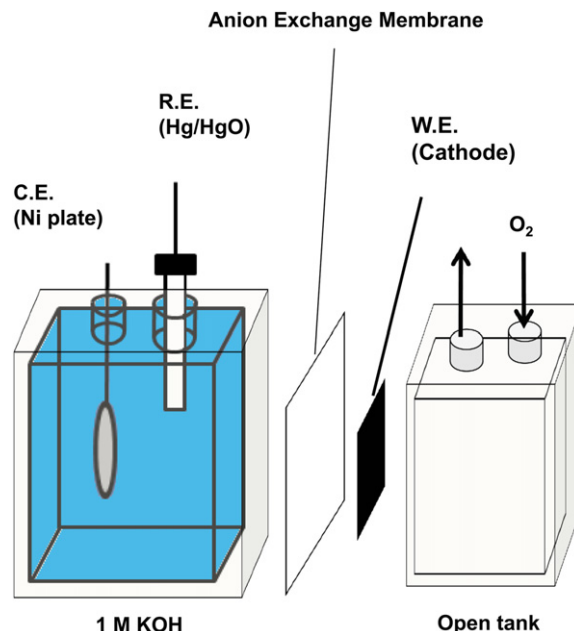

Fig. 1. Schematic representation of a half cell using an AEM.

with a weight ratio of 1:1:0.6. The optimum amount of ionomer should depend on the Pt catalyst loading in the catalyst layer. In the study on the influence of Nafion loading on performance of PEFC, the optimum amount of Nafion ionomer is reported to be about 0.8–1.1 mg cm^{-2} in the case of Pt loading amount of 0.4 mg cm^{-2} [24,25]. Although LDH crystals are rather easy to change shape and size, a formation of favorable contact interface with other electrode materials is rather difficult, compared with Nafion ionomer. In our experiment, the Pt loading amount is 1.9 mg cm^{-2}, the loading amount of LDH as ionomer was over 3.8–5.2 mg cm^{-2} for increasing TPB regions. Catalyst layers were formed by pasting catalyst ink on a carbon cloth (EC-CC1-T). ORR activity of fabricated electrodes in this way was evaluated in three electrode cell with 1 M KOH solution, and Hg/HgO electrode and Ni plate as reference and counter electrode, respectively. With the half cell, steady-state polarizations were measured at 5 mV s^{-1} in a potential range from −1.0 V to 0.2 V (v.s. Hg/HgO).

2.3. Fabrication of DEFC using catalyst layers with LDHs

A passive-type DEFC was fabricated using the AEM as an electrolyte, and the performance of DEFC was examined as described previously [13,15,16]. A nickel form and carbon cloth with non-Pt catalysts (Hypermec; ACTA S.p.A.) were used for the anode and cathode electrodes, respectively. These electrodes were prepared in the same way as described above. The loading amounts of the non-Pt catalysts are 1.9 mg cm^{-2}. The AEM was sandwiched with the two electrodes and the gold-plated current collectors that were attached with cell fixtures. An aqueous solution of ethanol and potassium hydroxide was used as fuel and the cathode was exposed to air. Polarization performances were measured using potentiostat and galvanostat (Autolab, PGSTAT30) at 80 °C.

3. Results and discussion

3.1. Characterization of Ni–Al CO_3^{2-} LDH and Mg–Al CO_3^{2-} LDH

The XRD patterns of resultant samples are shown in Fig. 2. The peaks at around 11° and 23° can be indexed as a rhombohedral structure, corresponding to (003), (006) planes of the LDH crystals.
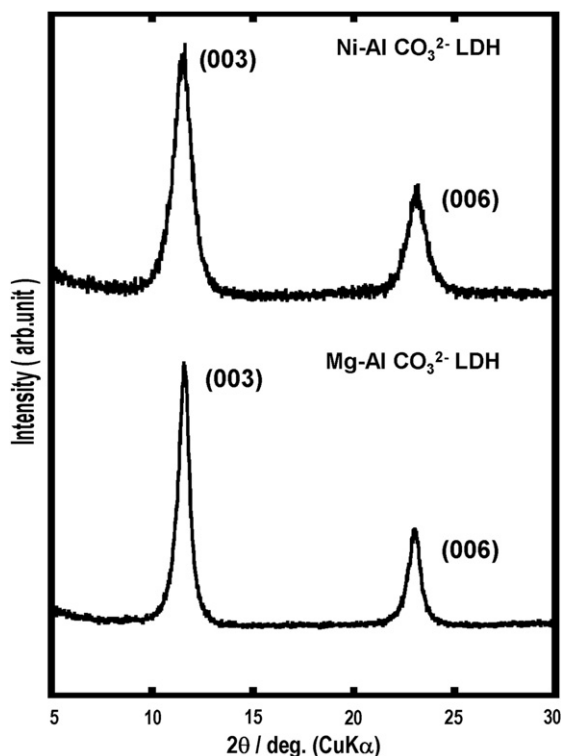
Fig. 2. XRD patterns of the obtained Ni–Al CO_3^{2-} LDH and Mg–Al CO_3^{2-} LDH.

Fig. 4. Temperature dependence of the ionic conductivity of Ni–Al CO_3^{2-} LDH and Mg–Al CO_3^{2-} LDH.

In the FT-IR spectra of these LDHs, a strong band at around 1350 cm^{-1}, which is attributed to C—O antisymmetric stretching of CO_3^{2-}, was observed, proving the presence of CO_3^{2-} in these LDHs. The typical morphology of the Ni–Al CO_3^{2-} LDH and Mg–Al CO_3^{2-} LDH powder, as observed by SEM, is illustrated in Fig. 3. The characteristic hexagonal plate-like morphology of LDHs was observed. The primary particle size of prepared LDHs was about 50–200 nm. This size must be favorable to be mixed well, because the size of LDH is similar to the size of carbon material loaded with catalyst for fuel cell. BET surface area analysis showed that specific surface area of Ni–Al CO_3^{2-} LDH and Mg–Al CO_3^{2-} LDH was 121 and 96 m^2 g^{-1}, respectively. These results suggested that Ni–Al CO_3^{2-} LDH and Mg–Al CO_3^{2-} LDH had similar characteristics.

Electrochemical properties of Ni–Al CO_3^{2-} LDH and Mg–Al CO_3^{2-} LDH were determined using the impedance spectroscopy. The behavior of Nyquist plots for these LDHs under humid condition were similar to that of previous report [14]. Temperature
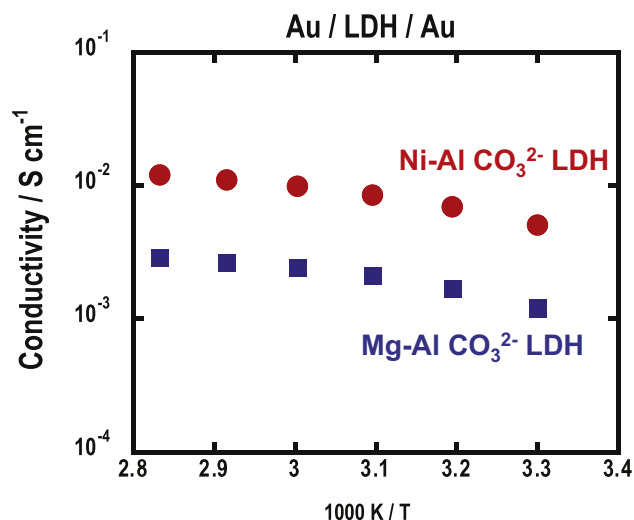
dependence of the conductivity for Ni–Al LDH and Mg–Al LDH under 80% relative humidity is shown in Fig. 4. The conductivity of Ni–Al CO_3^{2-} LDH is higher than that of Mg–Al CO_3^{2-} LDH. The electronic conductivity of Ni–Al CO_3^{2-} LDH (6 × 10^{-6} S cm^{-1}) is much lower than the conductivity of Ni–Al CO_3^{2-} LDH, indicating that Ni–Al CO_3^{2-} LDH is an ionic conductor. The result indicates that the divalent cation in LDH affects the ionic conductivity of LDH as described previously [14]. We also previously reported that the ionic conduction in LDHs is deeply related to the interlayer molecules, and the ionic conductivity of Ni–Al CO_3^{2-} LDH is higher than that of Ni–Al OH$^-$ LDH [16]. The interlayer molecules, which assumed to play an important role in ionic conduction, might be strongly held in the positively charged hydroxide layer of Ni–Al LDH. The factor must be related to the difference of the ionic conductivity in LDHs.

3.2. ORR activity of catalyst layers with LDHs

To investigate the effect of LDH addition as an ionomer to the catalyst layer, the ORR activity of catalyst layers consisted of Pt/C only, Pt/C + Ni–Al CO_3^{2-} LDH and Pt/C + Mg–Al CO_3^{2-} LDH was evaluated. The steady state polarization curves of the half cell using electrodes with different catalyst layers are shown in Fig. 5. The onset potential for ORR of the prepared catalyst layers was about 0 V (vs. Hg/HgO). The onset potential for ORR was unaffected by the
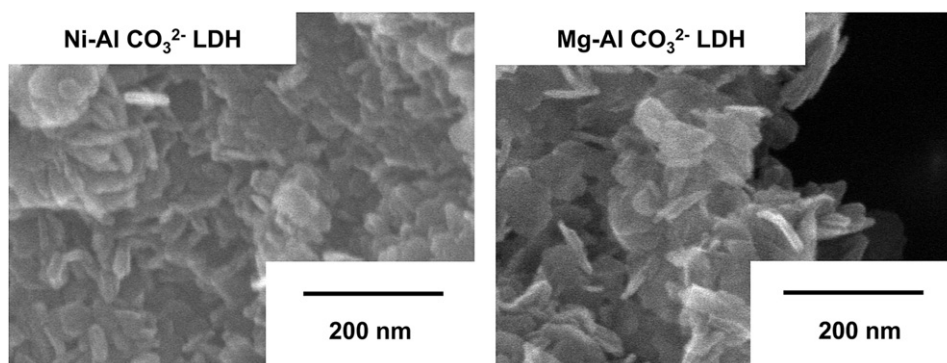

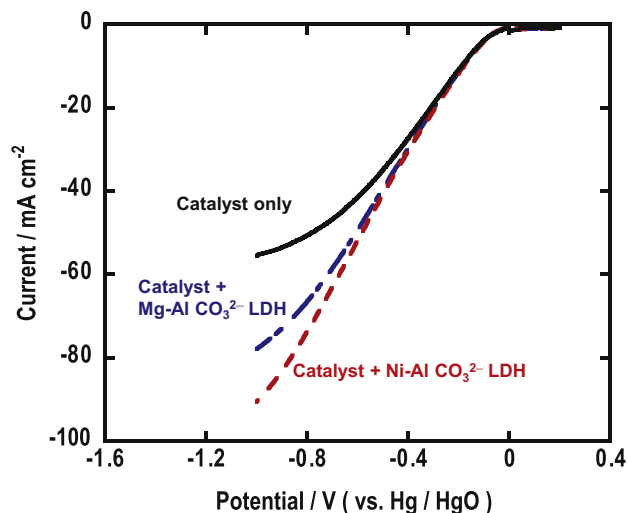Fig. 3. FE-SEM images of Ni–Al CO_3^{2-} LDH and Mg–Al CO_3^{2-} LDH.

Fig. 5. Steady-state polarization curves for the oxygen reduction reaction activity of the electrodes with LDHs or without LDH.

Fig. 6. Performance of the DEFC using the electrodes with LDHs as ionomer or without LDH, at 80 °C.

addition of LDHs to the catalyst layer. The current density for ORR below 0 V (vs. Hg/HgO) in the catalyst layers with LDHs was larger than that of catalyst layer without LDHs. The electrode containing Ni−Al CO_3^{2-} LDH showed the highest reduction current density. We previously reported that the predominant conducting ion species in Ni−Al CO_3^{2-} LDH and Mg−Al CO_3^{2-} LDH are hydroxide ions [13,14,16]. These results indicate that LDHs introduce OH$^-$ conducting paths in the catalyst layer and contribute to constructing more favorable TPB region. Ni−Al CO_3^{2-} LDH constructed more favorable TPB regions than Mg−Al CO_3^{2-} LDH because Ni−Al CO_3^{2-} LDH shows higher hydroxide ion conductivity. Miyazaki et al. investigated the effect of LDH addition to the catalyst layer [22], and showed that Mg−Al CO_3^{2-} LDH more effectively improved the performance of cathode than Ni−Al Cl$^-$ LDH. We reported that LDHs intercalated with CO_3^{2-} showed higher ionic conductivity than LDHs intercalated with Cl$^-$ [14,16]. In fact, Mg−Al CO_3^{2-} LDH showed higher ionic conductivity than Ni−Al Cl$^-$ LDH. In the present study, addition of Ni−Al CO_3^{2-} LDH to the catalyst layer is more effective than Mg−Al CO_3^{2-} LDH because the ionic conductivity of Ni−Al CO_3^{2-} LDH is higher than that of Mg−Al CO_3^{2-} LDH. In addition, LDHs containing transition metals can be electroactive materials. Thus, Ni−Al CO_3^{2-} LDH may have some catalytic activities for ORR and contribute to the improvement of the electrode performance.

3.3. Cell performance of DEFC using catalyst layer with LDHs

Alkaline-type DEFC using anion exchange membrane as an electrolyte and the prepared electrodes were fabricated to confirm the effect of LDH addition to the catalyst layer. Fig. 6 shows the cell performance for the passive-type alkaline DEFCs. DEFC performance test was conducted at relatively high temperature (80 °C) because the catalytic activity of ethanol is dependent on temperature. The DEFC using catalyst layers with LDHs showed higher cell performance than the DEFC using catalyst layer without LDH, in accordance with the obtained results for evaluation of ORR activity. The maximum power density of the DEFC using catalyst layer with Ni−Al CO_3^{2-} LDH was about 2 times higher than that using catalyst layer without LDH. The better performance was attributed to construction of more favorable TPB regions, which enhanced the electrode reactions and reduced activation overpotential.
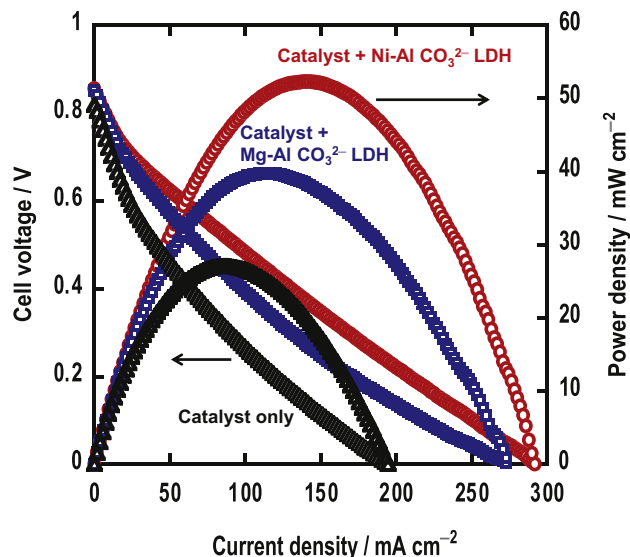
For the practical use of fuel cells, the formation of carbonate in AFCs, which cause the degradation of cell performance, should be resolved. The LDHs reported in this paper are carbonate salt. Therefore, the AFCs using LDH as alkaline fuel cell materials are not sensitive to the formation of carbonates. In this point of view, we believe that LDHs must be promising material in AFCs, and this type of AFC will have great potential for development for researches in AFCs.

4. Conclusions

The ORR activity of catalyst layers with LDHs was higher than that without LDH. The addition of Ni−Al CO_3^{2-} LDH more effectively increased the activity, because Ni−Al CO_3^{2-} LDH showed higher ionic conductivity than Mg−Al CO_3^{2-} LDH. The AFC using the prepared catalyst layers with LDHs showed a high performance. These results indicate that hydroxide ion conducting LDHs work as ionomer, and construct more favorable TPB regions in the catalyst layer.

Acknowledgment

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